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Pictures of Organic Molecules from X-ray Diffraction Data

By MAURICE L. HUGGINS*

ALTHOUGH the structures of many organic molecules have been deduced from x-ray diffraction data, only recently has a practical method been developed for obtaining pictures of molecules directly from such data. A procedure originally proposed and tried out by Sir Lawrence Bragg (*1*) has been modified and extended at the Kodak Research Laboratories in such a way as to enable one to obtain pictures in less than an hour of structures for which suitable x-ray data are available (*2*). It is true that the equivalents of such pictures in the form of contour maps of the structures could be obtained by calculational procedures, but these are long and tedious and require great care to avoid errors.

The first step in the process is to obtain a suitable x-ray diffraction photograph from a crystal of the substance being studied. By well-known methods, the diffraction spots are assigned indices, denoting the orientations of the reflecting planes in the crystal relative to the unit cell; the intensities of these spots are then measured, certain corrections are applied, and square roots are taken to arrive at "structure factors" that are independent of the shape of the crystal and the geometry of the x-ray setup. It is not always easy or possible to determine which square root, plus or minus, to take in each case.

The x-ray photograph does not look at all like the structure which produced it. From the list of indices and corresponding structure factors obtained from it, however, a second photographic step yields a picture of the crystal structure unit as viewed in a certain direction.

In this step, successive exposures onto a single sheet of photographic film or paper are made through certain masks—

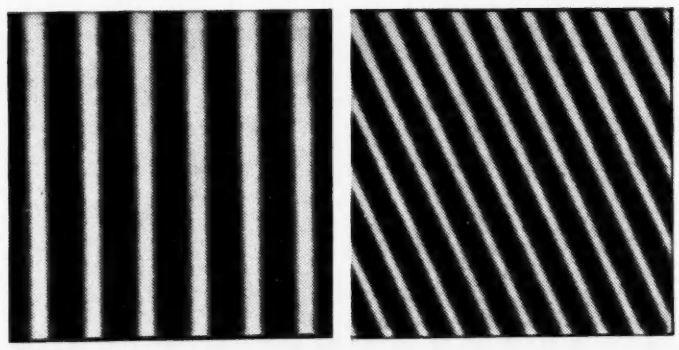

Figure 1

films having on them patterns of properly spaced and oriented bands such as those shown in Figure 1. The masks used are determined by the indices of the x-ray diffraction spots and the signs of the structure factors. The relative lengths of exposure are determined by the magnitudes of the structure factors. Development and fixation of the mul-

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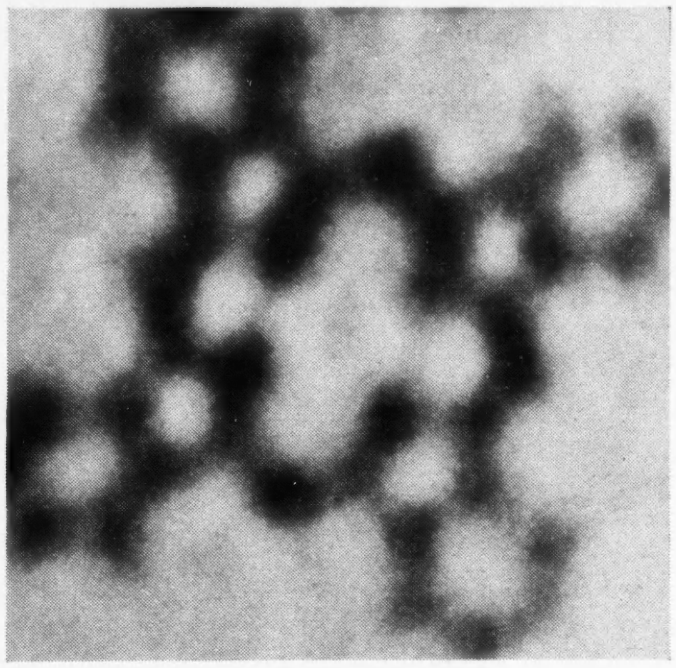

Figure 2

tiply-exposed film or paper yields the desired photograph.

If the crystal is of an organic substance, the unit cell, shown in the picture, may contain a single molecule or it may contain several. In many cases there is overlapping of different molecules. Frequently, the molecules are tilted relative to the plane of the picture. If the cross-section of the unit cell is not square, there will be some distortion on that account, though this can be removed, if desired, by a further step. In spite of these complications, however, this procedure is sure to prove of interest in presenting the results of crystal structure analysis, and of use in the working out of new structures.

An example of the sort of photograph obtained is shown in Figure 2. This shows a molecule of the dye phthalocyanine. The x-ray data used for this photograph were obtained by Robertson (*3*). It is seen that the carbon and nitrogen atoms show up fairly plainly, the hydrogens not at all (since their diffracting power for x-rays is negligible). The arrangement of atoms in the molecule is precisely that previously deduced by organic chemists.

References

(*1*) Bragg, W., Krist, X., *A70*, 475 (1929); also "The Crystalline State," Macmillan, London and New York (1934), Vol. I, p. 229.

(*2*) Huggins, M. L., *J. Am. Chem. Soc.*, 63, 66 (1941); *Science*, *100*, 570 (December 22, 1944); *J. Chem. Phys.*, *12*, 520 (December 1944); *Nature*, *155*; 18 (January 6, 1945).

(*3*) Robertson, J., *J. Chem. Soc.*, p. 1195 (1936).

A Quantitative Semimicro Hydrogenator

By E. M. SHANTZ*

THE organic chemist frequently needs to measure quantitatively the amount of hydrogen taken up during the catalytic reduction of a small amount of material. However, he is discouraged from constructing many of the various analytical hydrogenators described in the literature, for some of the following reasons: (1) a thermostatically controlled constant temperature bath is required; (2) a rotating ground joint or fragile glass coil connects the hydrogen source; (3) a multiplicity of stopcocks and ground joints which must be either hydrogen- or mercury-tight is incorporated into the design; and (4) very often the apparatus is so bulky that permanent laboratory space cannot be spared for it. The author has designed a semimicro hydrogenator which is simple to operate and is believed to overcome the objections mentioned. It has an accuracy of about 1% to 2% and requires samples of 50 to 300 mg.

Most of the details of the apparatus can be seen in Figure 1. It consists of two 200-ml. bulbs, *A* and *A'*, connected by an oblique bore stopcock, *B*. Each bulb is connected to a three-way manometer, *C*, whose third arm ends in a 1-mm. capillary stopcock, *D*, which can be opened to the atmosphere. Each bulb has a 19/38 standard taper ground-glass joint with stopper welded to its front at such an angle that the bulb may be rinsed and drained without disturbing

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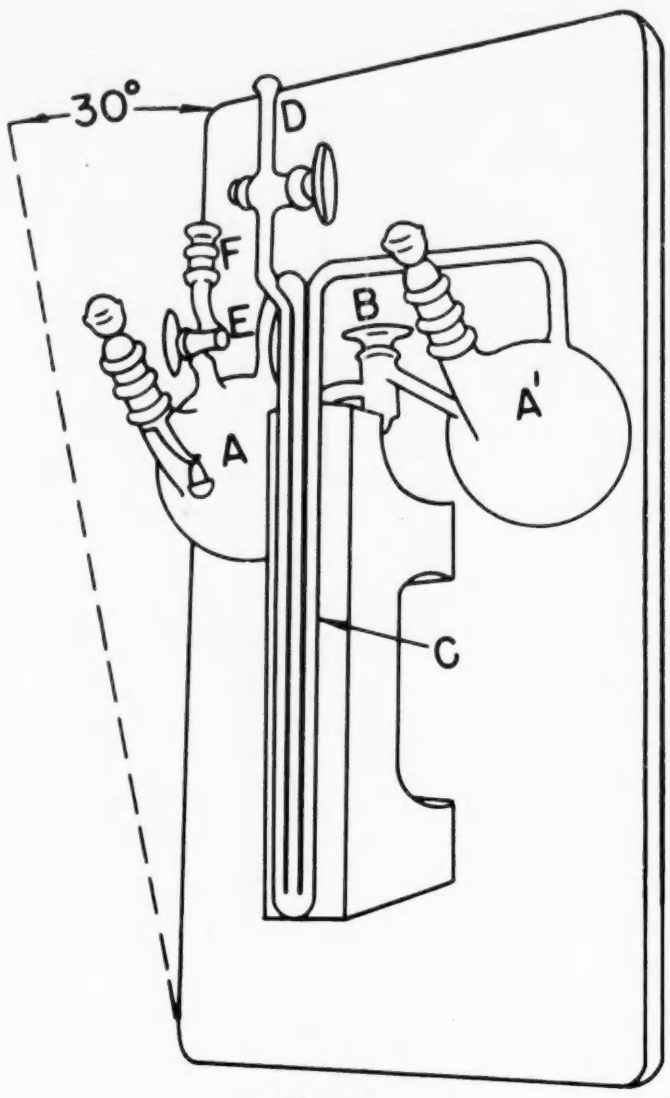

Figure 1

the mercury in the manometer. The stopper in the left-hand bulb has a glass hook upon which can be hung a small platinum bucket containing the sample. To this bulb is attached another oblique-bore stopcock, *E*, which is surmounted by a 10/30 ground-glass joint, *F*. The two halves are made to hold exactly equal volumes, so as to give complete temperature compensation. Two other accessories required are a two-way stopcock, *G* (Figure 2), whose single arm ends in a 10/30 ground-glass joint, and a 50-ml. burette tube (not shown) also having a 10/30 joint at the bottom. The apparatus may be fastened by small steel springs to a shaking board and then moved through a 30-degree arc (60 to 200 shakes per minute) by an eccentric driven by a 1/25 H.P. motor through a reducing pulley. The entire apparatus including a shaker of the type described can be stored in a space 24 inches high, 14 inches wide, and 20 inches deep.

In operating, the mercury is first drawn up by suction into the capillary of the open manometer arm, and stopcock *D* is closed. This is to prevent mercury from running into the bulbs when the system is evacuated. Equal amounts of solvent and catalyst are measured into each bulb and the weighed sample is placed on the hook in the left-hand side. The three-way stopcock *G* is placed in the ground joint *F*, with one arm connected to an aspirator or vacuum pump and the other to a hydrogen tank reducing valve opened at the lowest possible pressure. With stopcocks *B* and *E* open, the system is alternately evacuated and flushed with hydrogen six or eight times. Stopcock *E* is then closed, *G* is removed, and *D* is now opened. The pressure of the hydrogen is usually found to be about 10 mm. above atmospheric. If it is any higher, some of the hydrogen may be allowed to escape by carefully opening the two-way stopcock *E*.

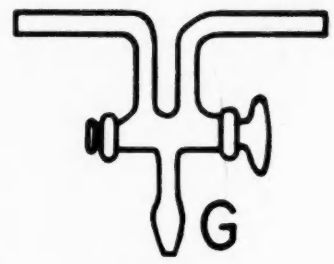

Figure 2

After standing for about one-half hour to come to equilibrium, the stopcock *B* is shut, the sample tipped from the hook, and shaken until no further change in pressure between the two bulbs is observed. The 50-ml. burette is now fitted into the joint *F* and filled with whatever solvent was used in the apparatus. After standing again until complete temperature equilibrium is reached, the solvent is slowly run into the bulb until the two sides are again at equal pressure. This volume is reduced to standard conditions after the barometric pressure has been corrected for both the vapor pressure of the solvent and for any observed difference between the apparatus and room pressure. The uptake of moles of hydrogen is then readily calculated.

Palladinized calcium carbonate has been found to be the best catalyst for

this work. The reduction of aliphatic carbon-carbon double bonds is completed in a few minutes. Aromatic double bonds are not reduced. Some results obtained on a few crystalline compounds are given below.

Compound	Wt. of Sample	Ml. H_2 (corrected)	Double Bonds	
			Found	Theory
Cinnamic Acid	0.1037 gm.	15.62	0.99	1.0*
Maleic Acid	0.2027 gm.	38.70	0.99	1.0
Maleic Acid	0.1601 gm.	30.73	0.99	1.0
Maleic Acid	0.1400 gm.	26.63	0.98	1.0
Carotene	0.2481 gm.	11.30	10.9	11.0
Carotene	0.3105 gm.	14.21	11.0	11.0

*Aliphatic

New Eastman Organic Chemicals

2554 Acridine MP 109-111° ..... 100 g... $4.70 C
$C_6H_4CH{:}C_6H_4{:}N$...MW 179.21

758 2-Amino-1,4-dimethylbenzene MP 10-13° ..... 100 g... 6.50 C
$NH_2C_6H_3(CH_3)_2$...MW 121.18

5548 4-Benzeneazo-1-naphthylamine MP 121-123° ..... 10 g... 2.50 A
$C_6H_5N{:}NC_{10}H_6NH_2$...MW 247.29

P 283 β-Bromostyrene (Pract.) MP −5° to 0° ..... 100 g... 4.00 C
$C_6H_5CH{:}CHBr$...MW 183.05

P 5529 3,4-Dichlorobenzoic Acid (Pract.) MP 201-202° ..... 1 kg... 5.00 E
$Cl_2C_6H_3COOH$...MW 191.02

5532 2,4-Dichlorophenoxyacetic Acid MP 138-140° ..... 100 g... 2.50 C
$Cl_2C_6H_3OCH_2COOH$...MW 221.04

5533 Disodium p-Nitrophenylphosphate ..... 1 g... 1.50 O
$NO_2C_6H_4OPO_3Na_2$...MW 266.07

5491 Ethyl N-Ethyl-N-phenylcarbamate BP 120-121°/7 mm. 100 g... 5.00 C
$C_2H_5N(C_6H_5)COOC_2H_5$...MW 193.24

5512 Fluoranthene MP 107-109° ..... 100 g... 2.00 C
$C_{16}H_{10}$...MW 202.24

P 5498 Hematoxylin Tetraacetate (Pract.) MP 144-150° dec...100 g... 3.00 C
$C_{24}H_{22}O_{10}$...MW 470.42

P 5520 2-Hexylpyridine (Pract.) BP 109-113°/19 mm.....500 g... 4.25 D
$CH_3(CH_2)_5C{:}NCH{:}CHCH{:}CH$...MW 163.25

P 5534 p-Nitrobenzenesulfonyl Chloride (Pract.) MP 74-79°...100 g... 2.50 C
$NO_2C_6H_4SO_2Cl$...MW 212.62

P 4593 Phenylacetone (Pract.) BP 100-101°/13 mm.....100 g... 3.00 C
$C_6H_5CH_2COCH_3$...MW 134.17

5527 Polyvinyl Hydrogen Phthalate.....500 g... 5.00 D